The Diffusional $CrevE_1CirrE_2C'$ Mechanism as a Unifying Electrochemical Platform for Coupled Chemical and Electrode Reactions

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Abstract

The diffusional $CrevE_1CirrE_2C'$ mechanism represents a comprehensive and unifying electrochemical framework capable of describing a remarkably broad spectrum of coupled electron-transfer and chemical reaction pathways encountered in modern electrochemistry. In this mechanism, all electroactive species are fully dissolved in solution and mass transport occurs exclusively by diffusion, while the interfacial electron-transfer steps are governed by Butler–Volmer kinetics. The mechanism incorporates a reversible preceding chemical equilibrium (Crev), two successive electrode reactions (E1 and E2), bridged by an irreversible homogeneous chemical transformation (Cirr), and a regenerative catalytic step (C′) coupled to the final product of second electrode transformation. Owing to this structural complexity, the model constitutes one of the most generalized diffusional reaction schemes ever treated theoretically within cyclic voltammetry.

In this work, the complete mathematical treatment of the diffusional $CrevE_1CirrE_2C'$ mechanism is established for the first time under cyclic voltammetric conditions by rigorous implementation of the Butler–Volmer formalism at the electrode interface. The proposed theoretical framework enables simulation and mechanistic interpretation of highly complex voltammetric responses that arise from the interplay between heterogeneous electron transfer, homogeneous kinetics, thermodynamic equilibria, and diffusional transport. Importantly, the model behaves as a genuine "all-in-one" mechanistic platform because numerous classical electrochemical mechanisms emerge as limiting cases under particular kinetic or thermodynamic conditions. Depending on parameter selection, the generalized scheme can converge toward simpler mechanisms such as E, EC, CE, ECirrE, CirrEC′, catalytic regenerative pathways, sequential ECirrEC' systems, and several other commonly encountered electrode mechanisms.

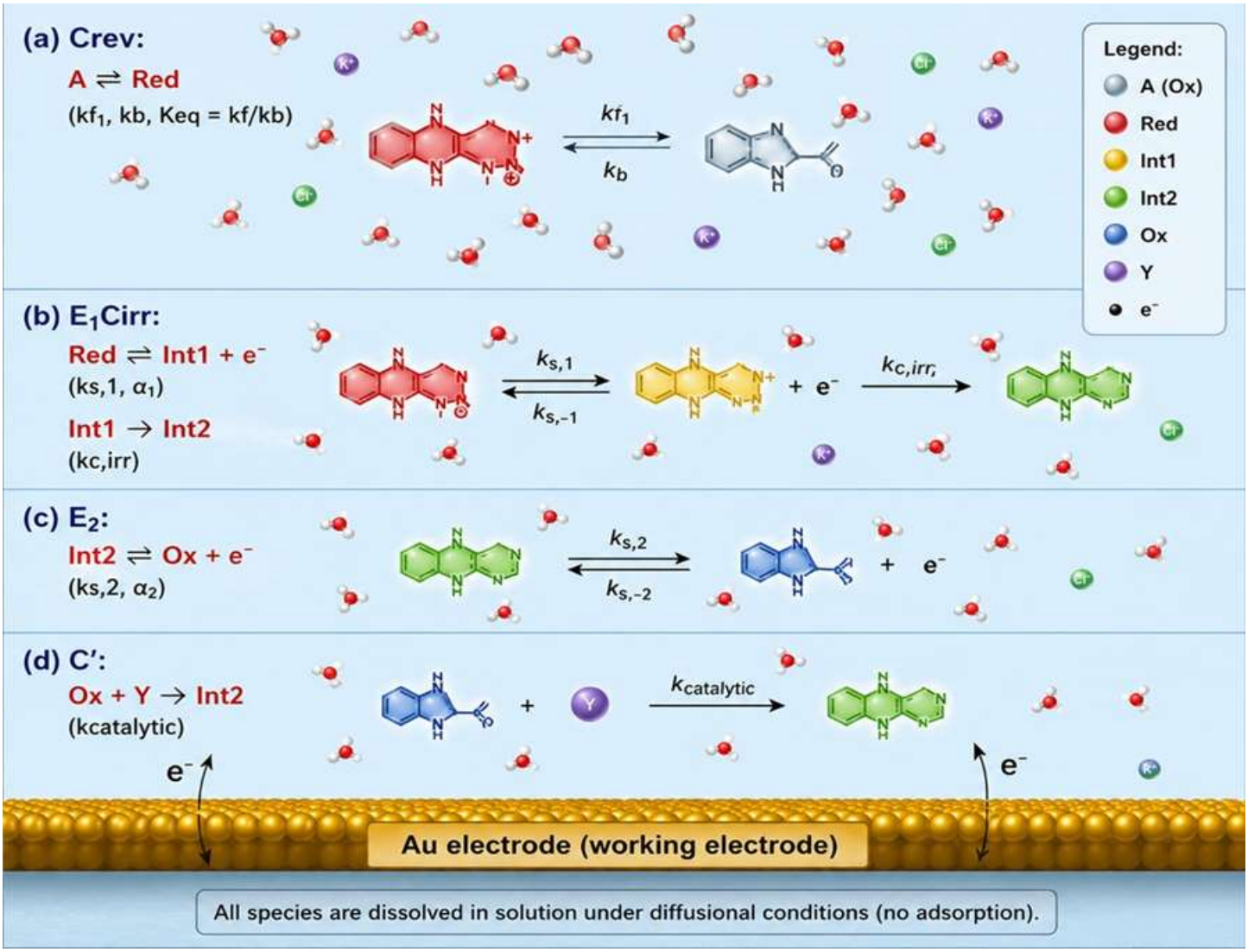
Consequently, this framework provides a unified theoretical language for interpreting a wide variety of experimentally observed voltammetric behaviors.

The practical significance of this generalized mechanism is considerable. Many biologically, catalytically, and industrially relevant electrochemical systems involve multiple coupled homogeneous and heterogeneous transformations that cannot be adequately described by simpler models. The present mechanism is therefore highly relevant for studying redox enzymes, catalytic mediators, transition-metal complexes, pharmaceutical compounds, bioelectrochemical systems, and multistep catalytic reactions. The framework offers the possibility to quantitatively analyze systems characterized by competing reversible and irreversible pathways, catalytic feedback loops, and kinetically controlled intermediate formation. Furthermore, because the model explicitly incorporates finite electron-transfer kinetics through Butler–Volmer relations, it enables realistic interpretation of quasireversible electrode processes frequently observed in experimental voltammetry.

The simulated voltammetric patterns are strongly influenced by several interconnected parameters. These include the standard rate constants of the electrode reactions ($k_{s,1}$ and $k_{s,2}$), electron-transfer coefficients ($\alpha 1$ and $\alpha 2$), scan rate, diffusion coefficients of all participating species, concentrations of reactants and catalytic agents, equilibrium constant of the preceding chemical step (Keq), rate constant of the reversible ($K_{chem1} = (k_f+k_b)\tau$) and that of irreversible chemical transformation ($K_{chem2}=k_{c,irr}\,\tau$), and the catalytic regeneration constant ($k_{catalytic}$). The interplay between these parameters determines peak positions, peak splitting, peak currents, wave asymmetry, appearance of catalytic plateaus, and the overall reversibility of the cyclic voltammograms. Variations in kinetic constants may induce dramatic transitions between reversible, quasireversible, irreversible, and catalytic voltammetric regimes, thereby generating highly diverse electrochemical signatures.

Beyond its scientific and mechanistic importance, the proposed model possesses exceptional educational value. Because it integrates virtually all fundamental electrochemical reaction pathways into a single theoretical framework, it can serve as a powerful pedagogical platform for teaching advanced electrode kinetics and mechanistic electrochemistry. Students and researchers can systematically explore how individual kinetic and thermodynamic parameters shape cyclic voltammetric responses and how complex mechanisms reduce to simpler limiting cases. In this sense, the model represents not only a significant theoretical advancement in

electrochemical science, but also a versatile educational tool for understanding the fundamental principles governing coupled electrochemical and chemical transformations. The mathematical approach and the entire simulation platform in Mathcad is available for free at: [Beyond Classical Electrochemical Mechanisms-For the First time Resolved the "Father" of all Electrode Mechanisms: The CrevECirrEC′ Diffusional Model as All-in-One Electrochemical Framework - UGD Academic Repository]



Reaction Scheme of CrevE1CirrE2C' mechanism unifying all common mechanistic pathways

References

1. R. Gulaboski, Journal of Solid State Electrochemistry 24 (2020) 2081-2081

2. R. Gulaboski, E. S. Ferreira, C. M. Pereira, M. N. D. S. Cordeiro, A. Garau, V. Lippolis, A. F. Silva, Journal of Physical Chemistry C 112 (2008) 153-161

3. V. Mirceski, M. Lovric, R. Gulaboski, Journal of Electroanalytical Chemistry 515 (2001) 91-100.

4. R. Gulaboski, V. Mirceski, Macedonian Journal of Chemistry and Chemical Engineering 39 (2020) 153-166

5. V. Mirceski, R. Gulaboski, Macedonian Journal of Chemistry and Chemical Engineering 33 (2014), 1-12

6. V. Mirceski, R. Gulaboski, Journal of Solid State Electrochemistry 7 (2003) 157-165

7. M. Janeva, P. Kokoskarova, V. Maksimova, R. Gulaboski, Electroanalysis 31 (2019) 2488-2506

8. R. Gulaboski, V. Mirceski, S. Komorsky-Lovric, M. Lovric, Electroanalysis 16 (2004) 832-842

9. R. Gulaboski, C.M. Pereira, M.N.D.S Cordeiro, I. Bogeski, F. Silva, Journal of Solid State Electrochemistry 9 (2005) 469-474

10. B. Sefer, R. Gulaboski, V. Mirceski, Journal of Solid State Electrochemistry 16 (2012) 2373-2381.

11. P. Kokoskarova, Rubin Gulaboski, Electroanalysis 32 (2020) 333-344.

https://doi.org/10.1002/elan.201900491

12. R. Gulaboski, C. M. Pereira, Electroanalytical Techniques and Instrumentation in Food Analysis; in Handbook of Food Analysis Instruments (2008) 379-402.

13. M. Jorge, R. Gulaboski, C. M. Pereira, M. N. D. S. Cordeiro, Journal of Physical Chemistry B 110 (2006) 12530-12538.

14. V. Mirceski, D. Guziejewski, L. Stojanov, R. Gulaboski, Analytical Chemistry 91 (2019) 14904-14910.

15. V. Mirceski, R. Gulaboski, F. Scholz, Journal of Electroanalytical Chemistry 566 (2004) 351-360.

16. R. Gulaboski, M. Chirea, C. M. Pereira, M. N. D. S. Cordeiro, R. B. Costa, A. F. Silva, J. Phys. Chem. C 112 (2008) 2428-2435

17. R. Gulaboski, V. Mirceski, S. Komorsky-Lovric, M. Lovric, Electroanalysis 16 (2004) 832-842

18. R. Gulaboski, C. M. Pereira, M. N. D. S. Cordeiro, A. F. Silva, M. Hoth, I. Bogeski, Cell Calcium 43 (2008) 615-621

19. R. Gulaboski, V. Mirceski, F. Scholz, Amino Acids 24 (2003) 149-154

20. V. Mirceski, R. Gulaboski, Croatica Chemica Acta 76 (2003) 37-48.

21. F. Scholz, R. Gulaboski, Faraday Discussions 129 (2005) 169-177.

22. R. Gulaboski, K. Caban. Z. Stojek, F. Scholz, Electrochemistry Communications 6 (2004) 215-218.

23. V. Mirceski, R. Gulaboski, Journal of Physical Chemistry B, 110 (2006) 2812-2820.

24. V. Mirceski, R. Gulaboski, B. Jordanoski, S. Komorsky-Lovric, Journal of Electroanalytical Chemistry, 490 (2000) 37-47.

25. R. Gulaboski, Macedonian Journal of Chemistry and Chemical Engineering 41 (2022) 151-162

26. R. Gulaboski, P. Kokoskarova, S. Petkovska, Analytical&Bioanalytical Electrochemistry, 12 (2020) 345-364.

27. V. Mirčeski, R. Gulaboski, F. Scholz, Electrochemistry Communications 4 (2002) 814-819

28. M. Jorge, R. Gulaboski, C. M. Pereira, M. N. D. S Cordeiro, Molecular Physics 104 (2006) 3627-3634.

29. R. Gulaboski, V. Mirceski, M. Lovric, Macedonian Journal of Chemistry and Chemical Engineering 40 (2021) 1-9.

30. R. Gulaboski, P. Kokoskarova, S. Risafova, J. Electroanal. Chem. 868 (2020) 114189.

31. R. Gulaboski, V. Mirceski, Journal of Solid State Electrochemistry 28 (2024) 1121-1130.

32. V. Mirceski, B. Mitrova, V. Ivanovski, N. Mitreska, A. Aleksovska, R. Gulaboski, Journal of Solid State Electrochemistry 19 (2015) 2331-2342.

33. I. Spirevska, L. Soptrajanova, R. Gulaboski, Analytical Letters 33 (2000) 919-928.

34. R. Gulaboski, B. Jordanoski, Bulletin of Chemists and Technologist of Macedonia 19 (2000) 177-181

35. R. Gulaboski, M. Lovrić, V. Mirčeski, I. Bogeski, M. Hoth, Biophysical Chemistry 137 (2008) 49-55.

36. R. Gulaboski, V. Mirčeski, S. Mitrev, Food Chemistry, 138 (2013) 116-121.

37. R. Gulaboski, V. Mirčeski, M. Lovrić, Journal of Solid State Electrochemistry 23 (2019) 2493-2506

38. V. Mirceski, R. Gulaboski, F. Scholz, Electrochemistry Communications 4 (2019) 814-819.

39. Rubin Gulaboski, V. Mirceski, Journal of Solid State Electrochemistry 28 (2024) 1121-1130.

40. R Gulaboski, F Borges, CM Pereira, M Cordeiro, J Garrido, AF Silva, Combinatorial chemistry & high throughput screening 10 (2007), 514-526

41. Rubin Gulaboski, Valentin Mirćeski, Carlos M Pereira, M Natalia DS Cordeiro, A Fernando Silva, François Quentel, Maurice L'Her, Milivoj Lovrić, *Langmuir*, 22 (2006) 3404-3412